

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 8/00, A61L 15/00	A1	(11) International Publication Number: WO 94/09043 (43) International Publication Date: 28 April 1994 (28.04.94)
(21) International Application Number: PCT/US93/09848		(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 14 October 1993 (14.10.93)		
(30) Priority data: 07/960,674 14 October 1992 (14.10.92) US 07/960,675 14 October 1992 (14.10.92) US 07/975,171 12 November 1992 (12.11.92) US		
(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(72) Inventor: GRAHAM, Andrew, T. ; 2214 East Wyllys Court, Midland, MI 48642 (US).		
(74) Agent: WARRICK, Noreen, D.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US).		

(54) Title: WATER-ABSORBENT POLYMER HAVING IMPROVED PROPERTIES

(57) Abstract

In one embodiment, the subject invention provides a surface-crosslinked water-absorbent polymer having improved properties and a process for its preparation. Through the use of a preferred primary crosslinking agent coupled with surface crosslinking, desirable absorptive properties are achieved. Suitable primary crosslinking agents include methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality. In another embodiment, the subject invention provides a process for preparing a water-absorbent polymer by the addition of a surface crosslinking agent to a hydrogel in the absence of a surfactant.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	CB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

WATER-ABSORBENT POLYMER HAVING IMPROVED PROPERTIES

The subject invention pertains to a surface-crosslinked water-absorbent polymer having improved properties. The subject invention further pertains to a process for preparing such a polymer. The subject invention further pertains to a method of using such a polymer.

Water-swellable polymers are used as constituents in personal care devices which absorb bodily fluids, such as sanitary napkins, incontinent devices and disposable baby diapers. Examples of such polymers are disclosed in U.S. Patent Nos. 3,926,891; 4,190,562; and 4,293,609.

Various processes are known for producing absorbent polymers. For example, U.S. Patent No. 4,833,222 teaches a process for preparing an absorbent polymer from a neutralized monomer with a surface-active agent. U.S. Patent No. 4,808,637 teaches the uniform reaction of acrylic acid, an alkali metal salt of carbonic acid, aluminum acetate, sodium sulfate and water, preferably using microwave radiation as a heat source to initiate polymerization.

Another process comprises the steps of preparing a reaction mixture consisting essentially of particular amounts of polymerizable acid group-containing monomers, crosslinking agent and optionally free radical initiator in an aqueous medium and thereafter polymerizing and neutralizing at least a portion of the acid functional groups.

Absorbent polymers used in personal care devices are characterized by certain performance properties, including centrifuge capacity, absorbence under load, shear modulus, and percent extractables.

U.S. Patent No. 4,666,983 discloses an absorbent article obtained by mixing 100 parts by weight of an absorbent resin powder having a carboxyl group with 0.0001 to 10 parts by weight of a crosslinking agent to crosslink the molecular chains existing at least in the vicinity of the surface of the absorbent resin powder.

U.S. Patent No. 4,734,478 discloses a water-absorbing resin powder having the molecular chains near its surface, the resin powder being obtained by mixing 100 parts by weight of a powder of a carboxyl-containing water-absorbing resin with 0.001 to 10 parts by weight of a polyhydric alcohol and heating the mixture at a temperature of at least 100°C to react the powder with the polyhydric alcohol, the improvement comprising conducting the mixing of the powder and the polyhydric alcohol in the presence of 0.01 to 8 parts by weight of a hydrophilic organic solvent and 0 to 8 parts by weight of water per 100 parts by weight of the powder.

Japanese Kokai Publication 84632/1981 discloses an absorption agent consisting of a crosslinked poly(alkali metal acrylate) material obtained from 0.01 to 10 parts by weight of a water-soluble and/or water dispersible surfactant and 0.005 to 20 parts by weight of a water-soluble polyvalent alcohol per 100 parts by weight of an acrylic acid/acrylate based polymer

composed of from 10-40 mole percent acrylic acid and 60-100 mole percent acrylate salt, wherein the polymer is formed by gel polymerization as a gel which is subsequently heated and dried.

European Patent Application 248,963 discloses a process of post treatment
5 wherein the surface of water-absorbent resin particles are treated with polyquaternary amines to significantly increase the absorption rate and to increase the absorption under load (AUL) by 10 percent. In the disclosed process, the polyquaternary amines are applied as solutions in methanol.

European Patent Application 248,437 discloses a process for post surface
10 crosslinking in which an aqueous solution of a water-soluble peroxide radical initiator is sprayed onto the surface of the water absorbent resin particles and the coated particles are heated. The reference alleges the achievement of additional surface crosslinking, leading to a product of improved water absorbency and water absorption rate. The reference discloses that the uniformity of penetration of the aqueous solution into the surface of the absorbent
15 polymer may be improved by using a water soluble organic solvent such as methanol. The disclosed process suffers the disadvantage of using high levels of peroxide free radical initiators, which discolors partly neutralized polyacrylic acid, making the product less appealing for personal care applications. The disclosed process suffers the further disadvantage of increasing the amount of extractable polymer, e.g., low molecular weight water-soluble
20 polymer, if the polymer is subjected to heat.

German Patent DE 3,713,601 discloses a process in which surface crosslinking is obtained by the addition of a crosslinker of glycidyl or polyglycidyl compounds. These crosslinking agents are not preferred in applications wherein the polymer is expected to contact human skin.

25 Industry would find great advantage in an aqueous fluid absorbent having improved absorbency under load and capacity. Industry would further find great advantage in a process for producing such an aqueous fluid absorbent

Accordingly, in one embodiment, the subject invention provides a water-absorbent polymeric material comprising a crosslinked polymer of a partially neutralized α,β-
30 ethylenically unsaturated monomer, the crosslinked polymer being crosslinked with a primary crosslinking agent selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality, or highly ethoxylated trimethylolpropane triacrylate, the crosslinked polymer being additionally crosslinked with a surface crosslinking
35 agent, whereupon the molecular chains existing in the vicinity of the surface of the polymer are crosslinked.

In another embodiment, the subject invention further provides a process for preparing an aqueous fluid absorbent material comprising:

- (a) preparing a crosslinked polymer of a partially neutralized α,β-ethylenically unsaturated monomer, the crosslinked polymer being crosslinked with a primary crosslinking agent selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality;
- 5 (b) contacting the crosslinked polymer with a surface crosslinking agent under conditions such that the surface crosslinking agent coats the crosslinked polymer without substantial penetration into the interior of the crosslinked polymer to form a coated crosslinked polymer; and
- 10 (c) heating the coated crosslinked polymer under conditions such that the surface crosslinking agent reacts with crosslinked polymer so as to crosslink the surface of the coated crosslinked polymer.

Through the unique combination of the preferred primary crosslinking agents expressed in the claims coupled with surface crosslinking, an improved balance of absorptive properties, e.g., absorption under load (AUL) and capacity, has been realized. The resultant compositions will afford high performance in any application in which aqueous fluid absorbents are used. In particular, the compositions of the subject invention will find great utility in personal care devices, where it is critical that the polymer have the capacity to hold substantial quantities of fluid, and retain such fluids upon the exertion of pressure, e.g., upon 20 sitting.

In another embodiment, the subject invention provides a process for preparing an aqueous fluid absorbent material comprising:

- (a) contacting a hydrogel comprising from 20 to 95 percent water-absorbent resin bearing carboxyl moieties and from 5 to 80 percent water with a composition comprising 25 a surface crosslinking agent in the absence of a surfactant, the composition optionally further comprising additional water and/or a water miscible polar solvent, under conditions such that the surface crosslinking agent coats the hydrogel without substantial penetration into the interior of absorbent resin particles of the hydrogel to form a coated hydrogel;
- (b) drying the coated hydrogel, such that the water, and optional additional 30 water and optional solvent if present, are substantially removed and such that the surface crosslinking agent does not significantly react with the carboxyl moieties to form a dried coated resin;
- (c) reducing the particle size of the dried coated resin by mechanical means to form dried coated particles; and
- 35 (d) heating the dried coated particles under conditions such that the surface crosslinking agent reacts with the carboxyl moieties so as to crosslink the surface of the dried coated particles.

These and other embodiments are more fully described in the following detailed description.

Generally, water absorbent resin particles are prepared by either a gel polymerization process or by a reverse suspension polymerization process, both of which are well-known.

In gel polymerization processes, monomers are polymerized in aqueous solution. Certain additives, such as crosslinking agents and surfactants, may be incorporated into the monomer mixture. The product of the polymerization process is a hydrogel, which is a water-swollen form of the polymer containing at least about 5 weight percent water. Generally, this hydrogel is subjected to mechanical means for reducing the particle size to granulate the hydrogel. Thereafter, the hydrogel is dried to remove the water. The particles are then typically subjected to further mechanical means of particle size reduction and classification including chopping, grinding, and sieving.

Surface crosslinked, as used herein, refers to absorbent resin polymer particles which are contacted with a crosslinking agent after completion of polymerization under conditions such that the particles are coated at or near the surface and the particles are exposed to conditions such that the surface crosslinking agent reacts with carboxyl groups at or near the surface of the particle to crosslink the water absorbent resin.

Hydrogel, as used herein, means water swollen absorbent resin particles. In preferred embodiments, such hydrogels comprise from 15 to 95 percent by weight water absorbent polymer, with the remainder comprising water. In a more preferred embodiment, the hydrogel comprises from 30 to 95 percent water absorbent polymer. In a most preferred embodiment, the hydrogel comprises from 80 to 95 percent water-absorbent polymer.

As will be set forth in greater detail below, the surface crosslinking agent may be applied at nearly any stage in the production process. For instance, the surface crosslinking agent may be applied to wet hydrogel exiting the reactor having a water content from 65 to 80 percent; to partially dried hydrogel having a water content between 15 and 35 percent; to more fully dried hydrogel having a water content between 5 and 15 percent; or to a polymer powder, having a water content less than about 5 percent.

The water-swellable or lightly crosslinked hydrophilic polymers that are usefully used in the present invention can be any of the known hydrophilic polymers which are capable of absorbing large quantities of fluids. In particular, water-absorbent polymers useful in this invention are water-absorbent polymers which contain carboxyl moieties. Preferably, at least about 0.01 equivalent of carboxyl groups are present per 100 grams of the water-absorbent resin.

Among preferred carboxyl-containing water absorbent polymers are hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of starch-acrylic acid graft copolymers, saponification products of vinyl acetate acrylic ester copolymers,

hydrolyzates of acrylonitrile copolymers, crosslinked products of hydrolyzates of acrylonitrile copolymers, hydrolyzates of acrylamide copolymers, crosslinked products of hydrolyzates of acrylamide copolymers, partially neutralized products of polyacrylic acids and crosslinked products of partially neutralized polyacrylic acids.

5 Examples of some suitable polymers and processes for preparing them are disclosed in U.S. Patent Nos. 3,997,484; 3,926,891; 3,935,099; 4,090,013; 4,093,776; 4,340,706; 4,446,261; 4,683,274; 4,459,396; 4,708,997; 4,076,663; and 4,190,562, the relevant portions of which are incorporated herein by reference. Such hydrophilic polymers are prepared from water-soluble α,β -ethylenically unsaturated monomers such as monocarboxylic acids,

10 polycarboxylic acids, acrylamide and their derivatives.

Suitable α,β -ethylenically unsaturated monomers include, for example, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid and alkali metal salts and ammonium salts thereof; maleic acid, fumaric acid, itaconic acid, acrylamide, methacrylamide and 2-acrylamido-2-methyl-1-propane sulfonic acid and its salts. The preferred monomers include acrylic acid and 15 methacrylic acid and their respective salt forms such as alkali metal or ammonium salts.

The water-soluble monomers useful in the present invention may be used in amounts ranging from 10 percent to 80 percent by weight based on the total weight of the aqueous monomer solution. Preferably, the amount ranges from 20 percent to 60 percent based on the total weight of the aqueous monomer solution.

20 Optionally, the minor amounts of other water-soluble, unsaturated monomers, such as alkyl esters of the acid monomers, e.g., methyl acrylate or methyl methacrylate may be present. In addition, certain grafting polymers, such as, for example, polyvinyl alcohol, starch and water soluble or swellable cellulose ethers may be employed to prepare products having superior properties. Such grafting polymers, when employed, are used in amounts up to about 25 10 weight percent based on the α,β -ethylenically unsaturated monomer. Further, it may be advantageous to include a chelating agent to remove trace metals from solution, e.g., when a metal reaction vessel is employed. One such chelating agent is VERSENEX V-80 (an aqueous solution of the pentasodium salt of diethylenetriamine pentacetic acid) (Trademark of The Dow Chemical Company). Such chelating agents, when employed, are generally used in 30 amounts between 100 and 2000 ppm based on the α,β -ethylenically unsaturated monomer.

It is desirable to obtain a level of conversion of monomer to polymer of at least about 95 percent. The polymerization may be carried out using acid monomers that are not neutralized or that have been neutralized or partially neutralized prior to the polymerization. Neutralization is conveniently achieved by contacting the aqueous monomer with an amount 35 of basic material sufficient to neutralize between 20 and 95 percent of the acid groups present in the acid monomers. Preferably, the amount of basic material will be sufficient to neutralize between 40 percent and 85 percent, and most preferably between 55 percent and 75 percent of the acid groups present in the acid monomers. When pre-neutralizing the monomer

solution, it is important to control the neutralization conditions so that the heat of neutralization does not cause the premature polymerization of the monomer mixture. The neutralization is advantageously carried out at temperatures below 40°C, preferably at temperatures below 35°C.

5 Compounds which are useful to neutralize the acid groups of the monomer are typically those which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Such compounds include alkali metal hydroxides, alkali metal carbonates and bicarbonates. Preferably, the material used to neutralize the monomer is sodium or potassium hydroxide or sodium carbonate or potassium carbonate. In determining 10 the desired degree of neutralization, care must be taken to ensure that the pH of the resulting crosslinked absorbent polymer, which will be contacted with or dispersed in an aqueous fluid to be absorbed, is maintained in a range appropriate for the applications for which the polymer is intended. Alternatively, the polymerization may be carried out employing unneutralized monomers and thereafter neutralizing, as is known in the art.

15 Conveniently, a conventional vinyl addition polymerization initiator is used in the polymerization of the water-soluble monomers and the crosslinking agent. A free radical polymerization initiator which is sufficiently soluble in the monomer solution to initiate polymerization is preferred. For example, water soluble persulfates such as potassium persulfate, ammonium persulfate, sodium persulfate, and other alkali-metal persulfates, 20 hydrogen peroxide and water soluble azo-compounds such as 2,2'-azobis (2-amidinopropane·HCl) may be used. Some of these initiators, such as hydrogen peroxide, can be combined with reducing substances such as sulfites or amines to form known redox type initiators. The total amount of initiators used may range from 0.01 to 1.0 weight percent, preferably 0.01 to 0.5 weight percent, based on the total weight of α,β-ethylenically 25 unsaturated monomer reactants.

The water-absorbent resin will preferably be lightly crosslinked to render it water-insoluble. The desired crosslinked structure may be obtained by the copolymerization of the selected water-soluble monomer and a crosslinking agent possessing at least two polymerizable double bonds in the molecular unit. The crosslinking agent is present in an 30 amount effective to crosslink the water-soluble polymer. The preferred amount of crosslinking agent is determined by the desired degree of absorption capacity and the desired strength to retain the absorbed fluid, i.e., the desired absorption under load (AUL). Typically, the crosslinking agent is used in amounts ranging from 0.0005 to 5 parts by weight per 100 parts by weight of α,β-ethylenically unsaturated monomer used. More preferably, the amount ranges 35 from 0.1 to 1 part by weight per 100 parts by weight of the α,β-ethylenically unsaturated monomer. If an amount over about 5 parts by weight of crosslinking agent per 100 parts is used, the resulting polymer has too high a crosslinking density and exhibits a reduced absorption capacity and increased strength to retain the absorbed fluid. If the crosslinking

agent is used in an amount less than about 0.0005 part by weight per 100 parts, the polymer has too low a crosslinking density, and when contacted with the fluid to be absorbed becomes sticky and exhibits a lower initial absorption rate.

While the crosslinking agent will typically be soluble in the aqueous solution of
5 the α,β -ethylenically unsaturated monomer, the crosslinking agent may be merely dispersible in such a solution, without negative implications. The use of such dispersing agents is disclosed in U.S. Patent No. 4,833,222. Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. Such dispersing agents are typically provided at a concentration between 0.005 and 0.1 weight
10 percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

Preferred crosslinking agents include trimethylolpropanetriacrylate, ethoxylated trimethylolpropanetriacrylate, butyleneglycoldiacrylate, ethyleneglycoldimethacrylate, ethylenebisacrylamide and diallylcarbonate, methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and difunctional monovinyl and monoallyl
15 esters and amides.

A certain class of crosslinking agents yields particularly preferred absorptive properties. Such preferred crosslinking agents include methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality. It has now been discovered that when polymers
20 prepared with the preferred crosslinking agents are further surface crosslinked with a polyhydroxy compound, absorptive properties are further improved.

Other crosslinking agents, such as highly ethoxylated trimethylolpropane triacrylate, when used to prepare a water-swellable polymer which is thereupon surface crosslinked, are expected to yield similar benefits in absorptive properties. Highly ethoxylated
25 trimethylolpropane triacrylate is a C₂₋₁₀ polyhydric hydrocarbon which has been ethoxylated with from two to eight ethylene oxide units per hydroxyl moiety of the ethylene oxide chain wherein the hydroxy moiety at the end of each chain is esterified with a C₂₋₁₀ unsaturated carboxylic acid or ester thereof. One example of highly ethoxylated trimethylolpropane triacrylate is trimethylol propane which has been ethoxylated with 2 to 7 ethylene oxide units
30 per hydroxy moiety and wherein each hydroxy moiety has been esterified with an acrylate moiety.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the α,β -ethylenically unsaturated monomer in the partially neutralized form, the crosslinking agent, the initiator and a grafting polymer substrate, if
35 desired, is prepared. The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Generally, the temperature at which polymerization will begin ranges from 20°C to 45°C. The temperature at which the polymerization is carried out is highly dependent

on the type of monomers used and the specific initiator system employed. Preferably, the maximum temperature of polymerization ranges from 50°C to 100°C, most preferably from 60°C to 100°C. The method by which the temperature of the polymerization is controlled is not critical so long as sufficient cooling is present to remove the heat which is generated during the 5 polymerization.

The resultant hydrogel typically contains from 20 to 35 weight percent water-absorbent polymer and from 65 to 80 percent water. The hydrogel is typically initially mechanically sized to form sized hydrogel particles having a reduced size prior to drying. Typically, such sized hydrogel particles have an average diameter less than about 2 cm.

10 The sized hydrogel particles are typically dried using means well-known in the art. Such drying means include fluidized bed driers, rotary driers, forced air ovens, through circulation band driers, etc. In some instances, drying will occur in two or more stages. In two-stage drying, the sized hydrogel particles are partially dried in the first stage, e.g., the size hydrogel particles are dried to less than 10 percent moisture level, preferably a 5 percent 15 moisture level. During the initial drying, the hydrogel particles tend to fuse together to form a sheet. In two-stage driers, the partially dried hydrogel sheets are broken to form pieces which are very roughly about 10 cm x 10 cm x 2 cm in dimension. Such pieces are then more fully dried in the second stage, e.g., are dried to a moisture level less than about 5 percent. Following the completion of drying the pieces are more fully sized to form particles having an average 20 diameter less than about 0.8 mm.

25 The polymer particles are surface crosslinked with a suitable surface crosslinking agent. Such crosslinking agents include polyhydroxyl compounds, polyglycidyl ether compounds, polyfunctional aziridine compounds, polyfunctional amine compounds and polyfunctional isocyanate compounds, with polyhydroxy compounds being especially preferred.

30 The polyhydroxy compound which is used as a surface crosslinking agent is a compound which contains at least two hydroxyl groups which are capable of readily reacting with the carboxyl groups of the water-absorbent resin of the hydrogel. Suitable polyhydroxy compounds will not volatilize or degrade at the temperature of heating. Preferably, the 35 polyhydroxy compound used in this invention is selected from the group consisting of glycol, diethylene glycol, triethylene glycol, polyethylene glycols, glycerol, polyglycerol, polyethoxylated glycerol, propylene glycol, polypropylene glycols, diethanolamine, triethanolamine, polyethylene oxide, propane diol, butane diol, hydroxy terminated oxyethylene-oxypropylene block copolymers, trimethylolpropane, pentaerythritol, sorbitol, mannitol, sugars, sugar derivatives, polyoxyethylene sorbitol derivatives, polyoxyethylenelanolin derivatives, polyethoxylated sorbitol lanolin derivatives and the like. More preferred polyhydroxy compounds include diethylene glycol, triethylene glycol, glycerol, polyethoxylated glycerol, polyethylene oxide, propylene glycol, trimethylolpropane,

agent is used in an amount less than about 0.0005 part by weight per 100 parts, the polymer has too low a crosslinking density, and when contacted with the fluid to be absorbed becomes sticky and exhibits a lower initial absorption rate.

While the crosslinking agent will typically be soluble in the aqueous solution of
5 the α,β -ethylenically unsaturated monomer, the crosslinking agent may be merely dispersible in such a solution, without negative implications. The use of such dispersing agents is disclosed in U.S. Patent No. 4,833,222. Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. Such dispersing agents are typically provided at a concentration between 0.005 and 0.1 weight
10 percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

Preferred crosslinking agents include trimethylopropanetriacrylate, ethoxylated trimethylopropanetriacrylate, butyleneglycoldiacrylate, ethyleneglycoldimethacrylate, ethylenebisacrylamide and diallylcarbonate, methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and difunctional monovinyl and monoallyl
15 esters and amides.

A certain class of crosslinking agents yields particularly preferred absorptive properties. Such preferred crosslinking agents include methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality. It has now been discovered that when polymers
20 prepared with the preferred crosslinking agents are further surface crosslinked with a polyhydroxy compound, absorptive properties are further improved.

Other crosslinking agents, such as highly ethoxylated trimethylopropane triacrylate, when used to prepare a water-swellable polymer which is thereupon surface crosslinked, are expected to yield similar benefits in absorptive properties. Highly ethoxylated
25 trimethylopropane triacrylate is a C₂-10 polyhydric hydrocarbon which has been ethoxylated with from two to eight ethylene oxide units per hydroxyl moiety of the ethylene oxide chain wherein the hydroxy moiety at the end of each chain is esterified with a C₂-10 unsaturated carboxylic acid or ester thereof. One example of highly ethoxylated trimethylopropane triacrylate is trimethylopropane which has been ethoxylated with 2 to 7 ethylene oxide units
30 per hydroxy moiety and wherein each hydroxy moiety has been esterified with an acrylate moiety.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the α,β -ethylenically unsaturated monomer in the partially neutralized form, the crosslinking agent, the initiator and a grafting polymer substrate, if
35 desired, is prepared. The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Generally, the temperature at which polymerization will begin ranges from 20°C to 45°C. The temperature at which the polymerization is carried out is highly dependent

on the type of monomers used and the specific initiator system employed. Preferably, the maximum temperature of polymerization ranges from 50°C to 100°C, most preferably from 60°C to 100°C. The method by which the temperature of the polymerization is controlled is not critical so long as sufficient cooling is present to remove the heat which is generated during the 5 polymerization.

The resultant hydrogel typically contains from 20 to 35 weight percent water-absorbent polymer and from 65 to 80 percent water. The hydrogel is typically initially mechanically sized to form sized hydrogel particles having a reduced size prior to drying. Typically, such sized hydrogel particles have an average diameter less than about 2 cm.

10 The sized hydrogel particles are typically dried using means well-known in the art. Such drying means include fluidized bed driers, rotary driers, forced air ovens, through circulation band driers, etc. In some instances, drying will occur in two or more stages. In two-stage drying, the sized hydrogel particles are partially dried in the first stage, e.g., the size hydrogel particles are dried to less than 10 percent moisture level, preferably a 5 percent 15 moisture level. During the initial drying, the hydrogel particles tend to fuse together to form a sheet. In two-stage driers, the partially dried hydrogel sheets are broken to form pieces which are very roughly about 10 cm x 10 cm x 2 cm in dimension. Such pieces are then more fully dried in the second stage, e.g., are dried to a moisture level less than about 5 percent. Following the completion of drying the pieces are more fully sized to form particles having an average 20 diameter less than about 0.8 mm.

25 The polymer particles are surface crosslinked with a suitable surface crosslinking agent. Such crosslinking agents include polyhydroxyl compounds, polyglycidyl ether compounds, polyfunctional aziridine compounds, polyfunctional amine compounds and polyfunctional isocyanate compounds, with polyhydroxy compounds being especially preferred.

30 The polyhydroxy compound which is used as a surface crosslinking agent is a compound which contains at least two hydroxyl groups which are capable of readily reacting with the carboxyl groups of the water-absorbent resin of the hydrogel. Suitable polyhydroxy compounds will not volatilize or degrade at the temperature of heating. Preferably, the polyhydroxy compound used in this invention is selected from the group consisting of glycol, diethylene glycol, triethylene glycol, polyethylene glycols, glycerol, polyglycerol, 35 polyethoxylated glycerol, propylene glycol, polypropylene glycols, diethanolamine, triethanolamine, polyethylene oxide, propane diol, butane diol, hydroxy terminated oxyethylene-oxypropylene block copolymers, trimethylolpropane, pentaerythritol, sorbitol, mannitol, sugars, sugar derivatives, polyoxyethylene sorbitol derivatives, polyoxyethylenolanolin derivatives, polyethoxylated sorbitol lanolin derivatives and the like. More preferred polyhydroxy compounds include diethylene glycol, triethylene glycol, glycerol, polyethoxylated glycerol, polyethylene oxide, propylene glycol, trimethylolpropane,

pentaerythritol, sorbitol, and polyethylene glycol. An especially preferred polyhydroxy compounds is glycerol.

Specific examples of the polyglycidyl ether compounds are ethylene glycol diglycidyl ether and glycerin diglycidyl ether.

5 Specific examples of the polyfunctional aziridine compounds are 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate], sold under the tradename Chemitite PZ-33; 1,6-hexamethylenediethyleneurea, sold under the tradename Chemitite HZ-22; and diphenylmethanebis-4,4'-N,N'-diethyloneurea, sold under the tradename Chemitite DZ-22, all of which are manufactured by Nippon Shokubai Kagaku Kogyo Co., Ltd.

10 Specific examples of the polyfunctional amines are ethylenediamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, and polyethyleneamine.

The surface crosslinking agent is present in an amount effective to crosslink the surface of the polymer. Such amount is determined by the desired capacity and AUL of the 15 final polymer. Ideally, such amount should significantly improve the gel strength of the polymer, as evidenced by an increased absorption under load (AUL), while not significantly reducing the capacity of the resin. Typically, the surface crosslinking agent is used in amounts ranging from 0.00002 to 10 parts by weight of the essentially dried absorbent resin product.

More preferably, the amount ranges from 0.0002 to 0.005 parts by weight per 1 part by weight 20 of dried absorbent resin product, i.e., from 200 to 5000 ppm based on the weight of the dried absorbent resin product. Preferably, the surface crosslinking agent will be provided in an amount of at least 300 ppm, more preferably at least 500 ppm, and more preferably at least 1000 ppm, and most preferably at least 3000 ppm based on the weight of the dried polymer.

The surface crosslinking agent may be applied at any stage of the production 25 process. For example, the surface crosslinking agent may be applied to the wet hydrogel exiting the reactor; to the partially dried hydrogel, e.g., to the gel having passed through the first stage of a two stage dryer; to more fully dried hydrogel, e.g., to the gel having passed through the second stage of a two stage dryer; to the polymer powder having a moisture content less than about 5 weight percent; or at any point in between.

30 Regardless of the point at which application of the surface crosslinking agent occurs, the surface crosslinking agent may be applied either neat, or in conjunction with water and/or an organic solvent. Preferably, the compositions containing the surface crosslinking agent will contain from 0 to 99 percent by weight water, from 0 to 50 percent organic solvent. More preferably, the compositions will contain from 0 to 50 percent water, and no organic 35 solvent. Most preferably, the compositions will contain no water and no organic solvent, i.e., the surface crosslinking agent will be applied neat.

Further, the composition containing the surface crosslinking agent may include a surfactant to facilitate a homogeneous distribution of the surface crosslinking agent on the

polymer particles, to improve the processability of the coated polymer particles, to reduce the tendency of the dried powder to agglomerate when exposed to humid air or water, and/or to bind fine dust of the water-absorbent resin.

The use of such surfactants is addressed in U.S. Serial No. 866,628, the relevant portions of which are incorporated herein by reference. Suitable surfactants are nonionic surfactants which are dispersible in water and which have an HLB value in the range of from 3 to 10. Preferred surfactants are those selected from the group of sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerol or polyglycerol fatty acid esters, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene acyl esters, and sucrose fatty acid esters or modified surface active polyesters.

Such surfactants are preferably used in an amount from 0.01 to 2 parts per 100 parts by weight of the water-absorbent resin, more preferably from 0.075 to 0.5 parts per 100 parts by weight of the water-absorbent resin.

When the surfactant has two or more hydroxyl moieties capable of reacting with carboxyl moieties, the surfactant can be used both as a polyhydroxy compound, e.g., surface crosslinking agent, and as a surfactant. In other words, certain polyhydroxy compounds which serve as surface crosslinking agents may also serve as surfactants. One example of such a polyhydroxy compound is a polyethoxylated sorbitol lanolin derivative.

The hydrogels/powders and the surface crosslinking agent should be contacted under conditions such that the particles can be coated with the surface crosslinking agent, but such that the surface crosslinking agent does not significantly diffuse into the internal structure of the water-absorbent resin particle. Preferably, such contacting will be conducted with some form of mechanical distribution, such that adequate distribution of the surface crosslinking agent on the water-absorbent resin particles occurs. Grinding, followed by moderate stirring, shaking, or even a short distance of conveying in a screw-conveyer is sufficient for such adequate distribution of the surface crosslinking agent over the hydrogel particles, particularly if the hydrogel particles are at an elevated temperature. For instance, neat surface crosslinking agent may be applied to the partially dried sized hydrogel particles exiting the first stage of a two-stage drier, whereupon the surface crosslinking agent is distributed over the surfaces of the particles during a mechanical sizing operation that occurs after the completion of drying but prior to heat treatment.

The temperature of contacting can be any temperature at which the surface crosslinking agent does not significantly react with the carboxyl moieties of the absorbent resin polymer. Such temperatures are typically at least from 20 to 150°C. It should be noted that elevated temperatures, i.e., those above ambient temperatures, improve the speed of coating of the hydrogel particles.

Upon application of the surface crosslinking agent to a hydrogel, the hydrogel is dried to a moisture level less than about 5 weight percent. Preferably, the hydrogel is dried to

a moisture level from 1 to 5 weight percent. Should the surface crosslinking agent be applied to the hydrogel prior to any drying, e.g., straight from the reactor, the drying will obviously require more time than should the surface crosslinking agent have been applied at some point downstream from the reactor, e.g., after passage through the first stage of a two-stage drier.

5 The temperature at which the drying takes place is a temperature high enough such that the water and any optional organic solvent is removed in a reasonable time period, yet not so high as to react the surface crosslinking agent with the carboxyl moieties of the water-absorbent resin. Preferably, the temperature of the water-absorbent resin particles during drying is about 170°C or less. More preferably, the temperature during drying is from
10 100 to 170°C, most preferably from 150 to 170°C.

The drying time should be sufficient to remove substantially all of the water and the optional solvent in a reasonable time period, and will depend on the drying system employed. Typically, the drying will reduce the moisture level of the hydrogel to a level from 1 to 5 weight percent.

15 The coated hydrogel will preferably be subjected to mechanical particle reduction means, e.g., chopping, cutting, and/or grinding. Such mechanical particle reduction means serve to reduce the particle size of the water-absorbent resin particles to a particle size acceptable in the ultimate end use. Such mechanical particle reduction will further preferably serve to distribute the surface crosslinking agent over the mechanically reduced particles. It is
20 for this reason that coating should precede and heat treatment should follow final sizing.

In a preferred mode, the coated absorbent resin particles are sized by first chopping, and then grinding. In a preferred embodiment, the resultant particle size is less than 2 mm, and is more preferably less than 0.8 mm. Preferably, the resultant particles have a size of at least 0.04 mm, more preferably at least 0.07 mm, and most preferably greater than 0.1 mm.

25 In the case wherein the surface crosslinking agent is applied to a powder, e.g., to a sized product having a moisture content less than about 5 weight percent, the surface crosslinking agent is applied with mixing by a ribbon mixer, screw mixer, fluidized bed mixer, V-shaped rotating mixer, etc. The mixed dried powder is then heat treated in the above manner. Application of the surface crosslinking agent, mixing, and heat treatment may advantageously
30 occur simultaneously, e.g., in the case of a fluidized bed mixer.

After drying and particle size reduction, the water-absorbent resin particles are subjected to conditions such that the polyhydroxy compound reacts with the carboxyl moieties of the water absorbent resin, so as to crosslink the water-absorbent resin at or near the surface of the particles. In particular, the dried and coated water-absorbent resin particles are heated
35 for a time sufficient to increase the modulus and/or the absorbency under load. Such heat treatment is preferably carried out at a temperature of at least about 170, more preferably of at least 180, and most preferably of at least about 190°C. Such heat treatment is preferably

carried out at a temperature of less than about 250, more preferably less than about 230, and most preferably less than about 210°C.

The time period for heat treatment should be sufficient for the surface crosslinking agent present at or near the surface of the absorbent resin to react with the carboxyl moieties. The exact times of heat treatment required will be affected by the equipment chosen, and can be determined empirically by examination of product properties. Preferably, the time is at least about 3 minutes, and more preferably at least about 5 minutes. If the time is too long, the process becomes uneconomical and a risk is run that the absorbent resin may be damaged. Preferably, the maximum time of heating is about 150 minutes or less, more preferably 60 minutes or less.

The method of heat treatment is not critical. For example, forced air ovens, fluidized bed heaters, heated screw conveyors, and the like may be successfully employed. If desired, the coated and heated polymer may be remoisturized for ease in handling.

While the subject invention has been described largely with respect to polymers prepared by gel polymerization processes, it should be recognized that the invention also applies to polymers prepared by suspension polymerization processes. For instance, an absorbent resin may be obtained by dispersing an aqueous solution of acrylic acid/acrylate containing a water-soluble free radical polymerization initiator and one of the primary crosslinking agents set forth above in an alicyclic and/or an aliphatic hydrocarbon solvent in the presence of a suspending aid, and subjecting the mixture to suspension polymerization. The resultant polymer beads are dried to remove residual solvent. The surface crosslinking agent is then applied to the dried beads with mixing, such as a ribbon mixer, a screw mixer, a rotating disc mixer, a fluidized bed mixer, a V-shaped rotating mixer, etc. The mixed dried beads are then heat treated in the manner specified above. Application of the surface crosslinking agent, mixing, and heat treatment may advantageously occur simultaneously, e.g., in the case of a fluidized bed mixer.

The following examples are provided for the purpose of explanation rather than limitation. Unless otherwise indicated, sixty minute 0.3 psi AUL was measured as described in European Patent Application EP 339,461-A1; sixty minute 0.6 psi AUL was measured in the manner described for the measurement of 0.3 psi AUL, except that a 0.6 psi pressure rather than a 0.3 psi pressure was applied and except that the test time was 90 minutes rather than 60 minutes; centrifuge capacity was determined as described in U.S. Patent 4,286,082 except that an absorption time of 30 minutes rather than 3 to 5 minutes was employed; fish eyes formation was determined as described in U.S. Patent No. 4,666,983; and the extractables and modulus were determined as described in U.S. Reissue Patent 32,649, with the relevant portions of each of the cited references being incorporated herein by reference. Further, vortex time was taken as the time for the vortex to disappear when 2 grams of polymer was added to 50 grams of a 0.9 percent saline solution contained in a 100 mL beaker while the saline solution was being

stirred with about a 1/2 to 1 inch vortex on a magnetic mixer. Gel blocking was noted in the vortex rate test if the powdered absorbent resin did not fully disperse into the saline solution. Percent moisture was determined by drying a portion of polymer at 135°C for about 60 hours, and using the weights before and after drying to calculate the percent moisture of the sample.

5 Example One

To a beaker, 300 grams of acrylic acid, 0.75 grams VERSENEX V-80 chelating agent (available from the Dow Chemical Company), 144 grams sodium carbonate, and enough water to bring the final reactor solids to 32 percent were added. To this, 145 grams of a 10 percent aqueous solution of polyvinyl alcohol was added and was thoroughly mixed. Then, 0.63 gram 10 allyl methacrylate was added. The resultant mixture was transferred to a reactor, which was purged with nitrogen to remove air. To the reactor, 4.8 mL of a 10 percent aqueous solution of sodium persulfate and 0.63 mL of a 30 percent aqueous solution of hydrogen peroxide were added. The contents of the reactor were mixed for one to two minutes. Then, 0.6 mL of a 10 percent aqueous solution of sodium erythorbate was added. Polymerization proceeded to 15 completion in about four hours.

The gel was dried in a standard commercial forced air oven. The majority of the particles of the dried resin mass were greater than 0.5 cm in length and breadth. When dry, a portion of the resin mass was ground and screened to pass through a 100 mesh sieve, and was saved as Comparative Example 1-A. A portion of the material of Comparative Example 1-A was 20 heat treated for 35 minutes at 210°C to form Comparative Example 1-B. The remainder of the unground and unscreened material was treated by weighing portions of the dried resin mass and weighing enough glycerine onto each portion to give the indicated amount of glycerin based on dry solids. Samples of each portion were ground and screened to pass through a 100 mesh sieve, and were heat treated for 35 minutes at 210°C to form Examples 1A and 1B.

25 The results of Examples 1A, 1B, and Comparative Examples 1-A and 1-B are set forth in Table One.

Example Two

To a beaker, 300 grams of acrylic acid, 0.75 grams VERSENEX V-80 chelating agent (available from the Dow Chemical Company), 144 grams sodium carbonate, and enough water 30 to bring the final reactor solids to 32 percent were added. To this, 145 grams of a 10 percent aqueous solution of polyvinyl alcohol was added and was thoroughly mixed. Then, 0.63 gram trimethylolpropanetriacrylate was added. The resultant mixture was transferred to a reactor, which was purged with nitrogen to remove air. To the reactor, 4.8 mL of a 10 percent aqueous solution of sodium persulfate and 0.63 mL of a 30 percent aqueous solution of hydrogen 35 peroxide were added. The contents of the reactor were mixed for one to two minutes. Then, 0.6 mL of a 10 percent aqueous solution of sodium erythorbate was added. Polymerization proceeded to completion in about four hours.

The gel was dried in a standard commercial forced air oven. The majority of the particles of the dried resin mass were greater than 0.5 cm in length and breadth. When dry, a portion of the resin mass was screened to be pass through a 100 mesh sieve and .. as saved as Comparative Example 2-A. A portion of the material of Comparative Example 2-A was heat
5 treated for 35 minutes at 210°C to form Comparative Example 2-B. The remainder of the unground and unscreened material was treated by weighing portions of the dried resin mass and weighing enough glycerine onto each portion to give the indicated amount of glycerin based on dry solids. Samples of each portion were ground and screened to pass through a 100 mesh sieve, and were heat treated for 35 minutes at 210°C to form Examples 2A and 2B.

10 The results of Examples 2A, 2B, and Comparative Examples 2-A and 2-B set forth in Table One.

15

20

25

30

35

TABLE ONE

Sample	Glycerine Concentration (ppm)	Fish Eyes	Vortex Time (sec)	Gel Block	30 sec capacity (g/g)	60 sec. capacity (g/g)	10 min. capacity (g/g)
Comparative 1-A	0	Yes	>200	Yes	6.3	9.9	21.4
Comparative 1-B	0	No	30	Yes			
1A	300	No	29	Yes	30.1	35.1	42.2
1B	3000	No	10	No	29.7	37.3	44.7
Comparative 2-A	0	Yes	>200	Yes	6.9	8.1	29.6
Comparative 2-B	0	No	140	Yes			
2A	300	No	17	No	28.4	35.0	42.9
2B	3000	No	11	No	29.9	37.3	42.8

Examples One and Two demonstrate that improved absorption rate and reduced fish eye formation and gel blocking can be obtained with a surface crosslinking agent is applied to the dry or partially dry absorbent resin polymer mass prior to grinding. The surface crosslinking agent can be applied in a range of at least from 300 to 3000 ppm, based on dry
5 solids.

Example Three

To a reactor, 48 pounds acrylic acid, 53.4 grams allyl methacrylate, 26.5 pounds of an 8 percent aqueous solution of VINOL 523 poly(vinyl alcohol) solution (available from Air Products Corp.), 22 pounds sodium carbonate, 98 pounds water, and 29 grams VERSENEX V-80
10 chelating agent were added and mixed. To the mixture, 37 grams sodium persulfate in an aqueous solution and 50.8 grams of a 30 percent aqueous solution of hydrogen peroxide were added and mixed. Next, 3.3 grams of sodium erythorbate in an aqueous solution were added. The reactor was then sparged with nitrogen. The polymerization began and was essentially complete in about 2 hours.

15 The resultant gel was separated into five parts for drying and coating with glycerin. Glycerin was added dropwise to the gel, at the drying stage extrapolated from the indicated percent moisture of the sample, in order to give about 500 ppm glycerine, based on the final dried weight of the polymer. When the glycerin was added to the polymer resin mass, samples of the resin mass were taken. Following addition of the glycerin, the samples were
20 dried to a moisture level of 5 percent and were ground and screened. A screen cut between 20 and 140 mesh was taken for use in capacity, AUL, and extractables determinations. A fines cut less than 140 mesh was taken for use in fish eye and vortex time determinations. The samples were heat treated in a commercial forced air oven for 40 minutes at 200°C, resulting in Examples 3A, 3B, 3C, 3D, and 3E. Comparative Example 3-A represents an uncoated, non-heat
25 treated sample of Example 3A. Comparative Example 3-B represents the uncoated sample of Comparative Example 3-A which has been heat treated.

The results of Examples 3A, 3B, 3C, 3D, 3E, and Comparative Examples 3-A and 3-B are set forth in Table Two.

Example Four:

To a reactor, 49 pounds acrylic acid, 37.7 grams trimethylolpropanetriacrylate, a solution of 22.5 pounds sodium carbonate in water, sufficient additional water such that the total amount of water equaled 115 pounds were added and mixed. To the mixture, 15 grams
5 VERSENEX V-80 chelating agent and 103 grams of a 5 percent aqueous solution of polyvinyl alcohol were added and mixed. To the mixture, 38.5 grams of sodium persulfate in an aqueous solution and 40 grams of a 30 percent aqueous solution of hydrogen peroxide were added and mixed. Next, 3.4 grams sodium erythorbate in an aqueous solution were added. The reactor was then sparged with nitrogen. The polymerization began and was essentially complete in
10 about 2 hours.

The resultant gel was separated into five parts for drying and coating with glycerin. Glycerin was added dropwise to the gel, at the drying stage extrapolated from the indicated percent moisture of the sample, in order to give about 500 ppm glycerine, based on the final dried weight of the polymer. At the time the glycerin was added to the polymer resin
15 mass, samples of the resin mass were taken. Following addition of the glycerin, the samples were dried to a moisture level of 5 percent and were ground and screened. A screen cut between 20 and 140 mesh was taken for use in capacity, AUL and extractables determinations. A fines cut less than 140 mesh was taken for use in fish eye and vortex time determinations. The samples were heat treated in a commercial forced air oven for 40 minutes at 200°C,
20 resulting in Examples 4A, 4B, 4C, 4D, and 4E. Comparative Example 4-A represents an uncoated, non-heat treated sample of Example 4A. Comparative Example 4-B represents the uncoated sample of Comparative Example 4-A which has been heat treated.

The results of Examples 4A, 4B, 4C, 4D, 4E, and Comparative Examples 4-A and 4-B are set forth in Table Two.

25

30

35

TABLE TWO

Sample	Percent Moisture	Fish Eyes	Vortex Time (sec)	Capacity	0.3 psi AUL	0.6 psi AUL	Percent Extractables
Comparative 3-A	5	Yes	>150	34.0	15.5	9.6	
Comparative 3-B	5			35.3	29.2	14.3	7.66
3A	5	No	13	34.4	29.9	18.0	7.96
3B	11.4	No	17	35.0	29.2	16.5	7.62
3C	59.5	No	17.5	34.6	29.8	18.1	7.64
3D	63	No	20	33.5	29.5	17.6	7.59
3E	202.5	No	17.5	34.1	30.0	18.3	7.64
Comparative 4-A	6.92	Yes	>150	44.3	7.9	8.4	17.59
Comparative 4-B	6.92			32.9	23.0	11.6	12.10
4A	6.92	No	15	30.9	25.1	16.9	12.39
4B	13.38	No	25	32.2	22.9	12.0	12.84
4C	37.4	No	24	31.3	24.0	13.4	12.08
4D	80.4	No	29	31.8	24.2	12.9	11.38
4E	208	No	27	33.4	22.5	10.9	11.91

Examples Three and Four demonstrate that the use of a preferred primary crosslinking agent improves the balance of absorptive properties and extractables, e.g., the ratio of 0.6 psi AUL to capacity increases while low levels of extractable polymer are maintained. Examples Three and Four demonstrate that, regardless of the primary 5 crosslinking agent employed, the surface crosslinking agent may be applied to gel of various moisture levels, such as wherein the gel comprises between 30 and 95 percent polymer, without sacrificing this balance of properties. Thus, the surface crosslinking agent may be directly added to the hydrogel prior to drying, without sacrificing polymer performance.

Example Five:

10 In a beaker, 300 grams acrylic acid 0.75 grams VERSENEX V-80 chelating agent, 144 grams sodium carbonate, and enough water to bring the final reactor solids to 32 percent were added and mixed. To the mixture, 145 grams of a 10 percent solution of poly(vinyl alcohol) was added and thoroughly mixed. Then, 0.9 grams allyl methacrylate was added, the mixture was added to a reactor, and the reactor was purged with nitrogen. To the reactor, 4.8 15 mL of a 10 percent aqueous solution of sodium persulfate and 0.63 mL of a 30 percent aqueous solution of hydrogen peroxide were added and mixed for one to two minutes. Then, 0.6 mL of a 10 percent solution of sodium erythorbate were added. The polymerization began and was completed in about 4 hours.

The resultant gel was separated into four parts and was dried in a standard 20 commercial forced air oven. When dry, one portion of the material was ground and saved as Comparative Example 5-1. Other portions of the material were treated by weighing the portions and weighing the indicated amount of glycerin onto the portions. The coated portions were placed in a food blender and were ground and screened to a 20 to 100 mesh cut. The sized and coated portions were placed in a jar and tumbled in a roller mixer for an 25 additional 15 to 30 minutes. The samples were then placed in a forced air oven at 200°C for 40 minutes to react the glycerin with the carboxyl groups on the absorbent resin. One of the sized portions was not coated with glycerin, but was heat treated as described, resulting in Comparative Example 5-2. The final products (Examples 5A, 5B, and 5C) and the products of the comparative examples were analyzed.

30 The results of Examples 5A, 5B, 5C, and Comparative Examples 5-1 and 5-2 are set forth in Table Three.

TABLE THREE

Polymer Sample	Glycerine (ppm)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	Swelling Capacity (g/g)	<u>AUL (0.6)</u> Swelling Cap
Comparative 5-1	0.0	10.0	9.1	36.4	0.25
Comparative 5-2	0.0	25.3	12.4	35.5	0.349
5A	286	26.2	16.3	34.0	0.479
5B	648	28.0	19.8	33.4	0.593
5C	1031	28.6	19.7	32.8	0.600

The difference between Comparative Examples 5-1 and 5-2 is typical of the way in which absorbent polymers made under these conditions react to heating. The effects of the surface treatment are found by comparing the results of Examples 5A through 5C. Some reduction in centrifuged capacity was observed. However, a slight increase in 0.3 psi AUL and a 5 substantial increase in 0.6 psi AUL likewise resulted. The improvement as a result of the present invention can be seen in the improvement in AUL/Swelling capacity in the rightmost column of Table Three.

Example Six:

Polymerizations were carried out in the same manner as described in Example 5, 10 excepting that the glycerin was replaced with the indicated coating material. Table Four lists the coating material (surface crosslinking agent), the amount of coating material used, and the product properties after heat treatment. Examples 6A, 6B, 6C, 6D and 6E are examples of the invention. Comparative examples 6-A1, 6-A2, 6-A3, 6-A4, and 6-A5 correspond to examples 6A, 6B, 6C, 6D and 6E, excepting that the comparative examples represent uncoated samples which 15 have not been heat treated. Comparative examples 6-B1, 6-B2, 6-B3, 6-B4, and 6-B5 correspond to examples 6A, 6B, 6C, 6D and 6E, excepting that the comparative examples represent uncoated samples which have been heat treated in the manner for heat treating the samples of Examples 6A, 6B, 6C, 6D and 6E. The final products (Examples 6A, 6B, 6C, 6D and 6E) and the products of the comparative examples were analyzed.

20 The results of Examples 6A, 6B, 6C, 6D, 6E, of Comparative Examples 6-A1, 6-A2, 6-A3, 6-A4, 6-A5, and of Comparative Examples 6-B1, 6-B2, 6-B3, 6-B4, and 6-B5 are set forth in Table Four.

25

30

35

TABLE FOUR

Sample	Surface Crosslinking Agent	Surface cross-linking agent amount (ppm)	0.3 psi AUL (g/g)	0.3 psi AUL (g/g)	Swelling Capacity (g/g)	Modulus (dynes/cm ²)	<u>0.6 psi AUL</u> Capacity
Comparative 6-A1	polyethylene oxide	0.0	13.6	9.0	33.1	22100	0.27
Comparative 6-A2		0.0	29.5	19.0	32.9	38300	0.57
6A	(avg. mol. wt = 200)	997	29.7	23.5	32.2	38700	0.72
Comparative 6-B1	polyethoxylated glycerol	0.0	9.9	8.5	35.4	22000	0.24
Comparative 6-B2		0.0	26.2	12.2	34.8	31500	0.35
6B	(avg. mol. wt = 212)	995	27.5	18.5	33.3	34200	0.55
Comparative 6-C1	propylene glycol	0.0	12.0	8.9	35.3	20200	0.25
Comparative 6-C2		0.0	23.8	12.1	34.5	28200	0.35
6C		1035	29.4	17.4	33.1	33800	0.52
Comparative 6-D1	polyethylene glycol	0.0	10.5	8.7	34.9	21300	0.25
Comparative 6-D2		0.0	26.6	13.5	33.9	34500	0.40
6D	(avg. mol. wt. = 600)	1991	26.7	16.4	33.8	34600	0.49
Comparative 6-E1	Sorbitol	0.0	16.9	9.1	32.9		0.28
Comparative 6-E2	(50% aqueous solution)	0.0	29.6	14.6	33.6		0.43
6E		501	29.8	18.5	33.5		0.55

The data set forth in Table Four illustrates that any polyfunctional alcohol containing material would be expected to perform satisfactorily in the process of the present invention.

Examples Seven and Eight:

5 In a beaker, 300 grams acrylic acid 0.75 grams VERSENEX V-80 chelating agent, 144 grams sodium carbonate, and enough water to bring the final reactor solids to 32 percent were added and mixed. To the reactor, the desired crosslinking agent was added. In the case of Example Seven, 0.95 grams methylenebisacrylamide crosslinking agent was added, the mixture was added to a reactor, and the reactor was purged with nitrogen. In the case of
10 Example Eight, 0.95 grams allyl methacrylate crosslinking agent was added, the mixture was added to a reactor, and the reactor was purged with nitrogen.

To the reactor, 4.8 mL of a 10 percent solution of sodium persulfate and 0.63 grams of a 30 percent solution of hydrogen peroxide were added and mixed for one to two minutes. Then, 0.6 grams of a 10 percent solution of sodium erythorbate were added. The
15 polymerization began and was completed in about 4 hours.

The resultant gels were each separated into two parts and were dried in a standard commercial forced air oven. When dry, one portion of each material was ground and saved as Comparative Examples 7-1, 7-2, 8-1 and 8-2. Other portions of the material were treated by weighing the portions and weighing the indicated amount of the surface
20 crosslinking agent onto the portions. The coated portions were placed in a food blender and were ground and screened to a 20 to 100 mesh cut. The sized products were coated with the indicated amount of coating material and were placed in a jar and tumbled in a roller mixer for an additional 15 to 30 minutes. The samples were then placed in a forced air oven at 200°C for
25 40 minutes to react the hydroxyl groups of the coating materials with the carboxyl groups on the absorbent resin. The final products (Examples 7A, 7B, 7C, 7D, 8A, 8B, 8C, and 8D) and the products of the comparative examples (7-1, 7-2, 8-1, and 8-2) were analyzed.

The results of Examples 7A, 7B, 7C, 7D, 8A, 8B, 8C, and 8D and comparative examples 7-1, 7-2, 8-1, and 8-2 are set forth in Table Five.

TABLE FIVE

Sample	Surface crosslinking agent	Surface cross-linking agent amount (ppm)	AUL g/g 0.3 psi	AUL g/g 0.6 psi	Swelling capacity g/g
Comparative 7-1		0	27.9	16.5	27.4
7A	Glycerine	533	30.0	26.7	29.6
Comparative 7-2		0	27.9	17.7	26.7
7B	polyethylene oxide (avg. mol. wt. = 200)	587	31.0	25.3	30.0
7C	Diethylene glycol	519	30.9	25.6	30.2
7D	polyethoxylated glycerol (avg. mol. wt. = 212)	542	31.2	25.9	30.1
Comparative 8-1		0	27.0	14.4	27.5
8A	Glycerine	505	30.3	26.3	29.1
Comparative 8-2		0	26.8	18.9	26.3
8B	polyethylene oxide (avg. mol. wt. = 200)	536	29.9	24.0	28.9
8C	Diethylene glycol	520	29.5	23.8	28.9
8D	polyethoxylated glycerol (avg. mol. wt. = 212)	522	29.5	24.2	28.8

The data set forth in Table Five illustrates that polymers of the subject invention which are free of poly(vinyl alcohol) which utilize allyl methacrylate and/or methylenebisacrylamide type crosslinking agents, result in polymers having very desirable absorptive properties.

5 Example Nine:

Polymerizations were conducted in the same manner as described with respect to Example 5, except that the coating material was a mixture of glycerine and water as shown in Table Six to make absorbent resins 9A, 9B, and 9C. Comparative Example 9-1 is a heat treated uncoated sample.

10 The results of Examples 9A, 9B, 9C and comparative example 9-1 are set forth in Table Six.

15

20

25

30

35

TABLE SIX

Sample	Coating Composition	Glycerine amount (ppm)	AUL g/g 0.3 psi	AUL g/g 0.6 psi	Swelling Capacity g/g
Comparative 9-1		0.0	23.9	12.2	36.8
9A	80% Glycerine	514	26.6	16.9	34.2
9B	65% Glycerine	501	27.2	19.2	34.0
9C	50% Glycerine	500	27.2	16.7	34.8

The data set forth in Table Six illustrates that while the presence of water as a solvent for the coating material is not necessarily beneficial, at the levels indicated here, it does not harm the spread of the coating chemical over the surface of the absorbent resin. Despite the presence of water, the improved combination of swelling capacity and AUL of the present invention is observed.

5 Example Ten:

In a beaker, 310 grams of acrylic acid, 0.75 grams VERSENEX V-80 chelating agent, 144 grams sodium carbonate, and enough water to bring the final reactor solids to 32 percent were added and mixed. Then 0.10 grams allyl methacrylate was added, the mixture was added 10 to a reactor, and the reactor was purged with nitrogen. To the reactor, 4.8 mL of a 10 percent solution of sodium persulfate and 0.63 mL of a 30 percent solution of hydrogen peroxide were added and mixed for one to two minutes. Then, 0.6 mL grams of a 10 percent solution of sodium erythorbate were added. The polymerization began and was completed in about 4 hours.

15 The resultant gels were dried in a standard commercial forced air oven. When dry, one portion of each material was ground and saved as Comparative Examples 10-A1, 10-B1, and 10-C1. The dried products were treated by weighing the dried resin masses, and weighing enough glycerine onto the dried resin masses to give about 500 ppm glycerin based on dry solids. The products were ground to 20 to 100 mesh, were placed in jars, and were 20 tumbled in a roller mixer for an additional 15 to 30 minutes. Portions of the materials were heat treated in a forced air oven for times and at the temperatures indicated in Table Seven. The final products and the products of the comparative examples were analyzed.

25 The results of Examples 10A1, 10A2, 10A3, 10A4, 10A5, 10A6, Examples 10B1, 10B2, 10B3, 10B4, 10B5, 10B6, Examples 10C1, 10C2, 10C3, 10C4, 10C5, 10C6, and Comparative Examples 10-A1, 10-B1, and 10-C1 are set forth in Table Seven.

30

35

TABLE SEVEN

Sample	Heating Temp.	Heating Time	AUL g/g 0.3 psi	AUL g/g 0.6 psi	Swelling Capacity g/g
Comparative 10-A1	200	35 min	14.4	9.4	37.8
	180	0	13.0	8.9	33.5
	10A2	15 min	17.7	10.0	34.3
	10A3	30 min	24.9	12.1	34.1
	10A4	45 min	27.5	13.0	34.0
	10A5	60 min	27.3	13.4	34.2
Comparative 10-B1	200	35 min	9.4	8.5	42.5
	190	0	9.2	8.5	36.8
	10B2	15 min	17.9	9.5	37.6
	10B3	30 min	21.3	10.0	38.4
	10B4	45 min	21.2	9.6	38.4
	10B5	60 min	21.5	9.6	38.6
Comparative 10-C1	200	35 min	10.1	9.1	39.4
	200	0	9.7	8.3	35.8
	10C2	10 min	22.7	10.8	36.3
	10C3	20 min	23.6	11.0	37.0
	10C4	30 min	23.4	10.9	37.0
	10C5	40 min	24.2	10.6	37.2
10C6		50 min	26.0	13.0	36.8

Example Ten demonstrates the applicability of heat treating temperatures between 180 and 200°C in the practice of the subject invention. Example Ten further demonstrates the shift in product properties that occurs as a function of the time for heat treatment.

Example Eleven:

1900 kg of acrylic acid, 4.56 kg of trimethylolpropanetriacrylate, 475 grams of polyvinyl alcohol, 950 grams of VERSENEX V-80 chelating agent, and 1435 kg of a 50 percent aqueous solution of sodium hydroxide were combined in a vessel with enough additional

water to bring the final polymer solids concentration to 35 percent. Sodium persulfate and hydrogen peroxide were added and the mixture was purged with nitrogen to remove air. A solution of ascorbic acid was added and the polymerization proceeded to completion in about 2 hours. The resultant gel was dried in a standard commercial forced air oven and was ground.

5 A portion of the polymer was weighed into a container, and to it was added 250 grams of an 80/20 propanol/water solution containing glycerine, such that the weight of glycerine to the weight of polymer was 0.2 percent. This material was dried overnight at 100°C. Subsequently, this material was dried in an open glass container in a 180°C oven for 40 minutes. The 0.3 psi AUL was 31.7 g/g, the centrifuge capacity was 36.1 g/g, and the 16 hour extractables were 14

10 percent.

Example Twelve:

A polymerization is conducted in the same manner as described in Example Five. The gel is dried and ground using a food blender and screened to a 20 to 100 mesh cut. Glycerin is added to the powder at a 500 ppm level. The sample is tumbled for 15 to 20 minutes 15 on a roller mixer. The samples are then placed in a forced air oven at 200°C for 40 minutes. The 0.3 psi AUL is about 30 g/g, the centrifuge capacity is about 35 g/g and the 16 hour extractables are about 8 percent. This demonstrates that the surface crosslinking agent may be applied to the sized polymer powder without sacrificing the balance of absorptive properties afforded by the subject invention.

20

25

30

35

CLAIMS

1. A water-absorbent polymeric material comprising a crosslinked polymer of a partially neutralized α,β -ethylenically unsaturated monomer, the crosslinked polymer being crosslinked with a primary crosslinking agent selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl 5 methacrylate and esters or amides having both a vinyl and an allyl functionality, or highly ethoxylated trimethylolpropane triacrylate, the crosslinked polymer being additionally crosslinked with a surface crosslinking agent, whereupon the molecular chains existing in the vicinity of the surface of the polymer are crosslinked.
- 10 2. The water-absorbent polymeric material of Claim 1, wherein the surface crosslinking agent is a polyhydroxy compound.
- 15 3. The water-absorbent polymeric material of Claim 2, wherein the polyhydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, glycerol, propylene glycol, trimethylolpropane, pentaerythritol, sorbitol, and polyethylene glycol.
- 20 4. The water-absorbent polymeric material of Claim 2, wherein the polyhydroxy compound is glycerol.
- 25 5. The water-absorbent polymeric material of Claim 1, wherein the primary crosslinking agent is allyl methacrylate.
- 30 6. The water-absorbent polymeric material of Claim 1, wherein the surface crosslinking agent is provided in an amount from 0.00025 to 2 weight percent, based on the weight of the crosslinked polymer.
- 35 7. A process for preparing an aqueous fluid absorbent material comprising:
 - (a) preparing a crosslinked polymer of a partially neutralized α,β -ethylenically unsaturated monomer, the crosslinked polymer being crosslinked with a primary crosslinking agent selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate and esters or amides having both a vinyl and an allyl functionality;
 - (b) contacting the crosslinked polymer with a surface crosslinking agent under conditions such that the surface crosslinking agent coats the crosslinked polymer without substantial penetration into the interior of the crosslinked polymer to form a coated crosslinked polymer; and
 - (c) heating the coated crosslinked polymer under conditions such that the surface crosslinking agent reacts with crosslinked polymer so as to crosslink the surface of the coated crosslinked polymer.
- 40 8. The process of Claim 7, wherein the crosslinked polymer exists as a hydrogel comprising from 20 to 95 percent crosslinked polymer and from 5 to 80 percent water at the contacting of step (b).

9. The process of Claim 7, wherein the process further comprises:

- (d) drying the coated crosslinked polymer, such that the water retained within the hydrogel is at least partially removed but such that the surface crosslinking agent does not react with the coated crosslinked polymer, the drying occurring after the contacting of step (b) 5 but prior to the heating of step (c).

10. The process of Claim 7, wherein the process further comprises:

- (d) drying the crosslinked polymer to a moisture content less than about 15 percent prior to the contacting of step (b).

11. The process of either of Claims 9 or 10, wherein the process further 10 comprises:

- (e) reducing the particle size of the coated crosslinked polymer by mechanical means after the drying of step (d) but before the heating of step (c).

12. The process of Claim 7, wherein the crosslinked polymer exists as a powder having a moisture content less than about 5 weight percent at the contacting of step (b).

13. A process for preparing an aqueous fluid absorbent material comprising:

(a) contacting a hydrogel comprising from 20 to 95 percent water-absorbent resin bearing carboxyl moieties and from 5 to 80 percent water with a composition comprising a surface crosslinking agent in the absence of a surfactant, the composition optionally further comprising additional water and/or a water miscible polar solvent, under conditions such that 20 the surface crosslinking agent coats the hydrogel without substantial penetration into the interior of absorbent resin particles of the hydrogel to form a coated hydrogel;

(b) drying the coated hydrogel, such that the water, and optional additional water and optional solvent if present, are substantially removed and such that the surface crosslinking agent does not significantly react with the carboxyl moieties to form a dried 25 coated resin;

(c) reducing the particle size of the dried coated resin by mechanical means to form dried coated particles; and

(d) heating the dried coated particles under conditions such that the surface crosslinking agent reacts with the carboxyl moieties so as to crosslink the surface of the dried 30 coated particles.

14. The process of Claim 13, wherein the drying of step (b) results in a dried coated resin having a water content less than about 10 percent.

15. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is provided in a composition which comprises the surface crosslinking agent, and which 35 optionally contains one or more constituents selected from the group consisting of water, an organic solvent, and a surfactant.

16. The process of either of Claims 7 or 13, wherein the composition comprises from 50 to 100 percent polyhydroxy compound and from 0 to 50 percent water, the composition being free from organic solvent.

17. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is a polyhydroxy compound.

18. The process of either of Claims 7 or 13, wherein the polyhydroxy compound is selected from the group consisting of diethylene glycol, triethylene glycol, glycerol, propylene glycol, trimethylolpropane, pentaerythritol, sorbitol, and polyethylene glycol.

19. The process of either of Claims 7 or 13, wherein the polyhydroxy compound is glycerol.

20. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is provided at a level of at least about 200 ppm based on the weight of the water-absorbent resin.

21. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is provided at a level of at least about 500 ppm based on the weight of the water-absorbent resin.

22. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is provided at a level of at least about 1000 ppm based on the weight of the water-absorbent resin.

23. The process of either of Claims 7 or 13, wherein the surface crosslinking agent is provided at a level of at least about 3000 ppm based on the weight of the water-absorbent resin.

24. The process of Claim 8, wherein the heating occurs at a temperature from 175 to 230°C for from 5 to 75 minutes.

25. An aqueous fluid absorbent material produced in accordance with the process of either of Claims 7 or 13.

26. A method for using the aqueous fluid absorbent material of either of Claims 1 or 22, comprising incorporating the absorbent material into a personal care device.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/09848

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F8/00 A61L15/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A61L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 317 106 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.) 24 May 1989 see page 3, line 17 - line 55 see page 4, line 27 - line 43; claims 1-10; examples 1,7 ---	1-26
A	EP,A,0 248 437 (HAYASHIKANE SHIPBUILDING & ENGINEERING CO., LTD.) 9 December 1987 cited in the application see claims 1-20 ---	1
A	GB,A,2 155 020 (KAO CORPORATION) 18 September 1985 see claims 1,2 ---	1
A	EP,A,0 450 924 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.) 9 October 1991 see claims 1-20 ---	1
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

2

Date of the actual completion of the international search

18 February 1994

Date of mailing of the international search report

18. 03. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

INTERNATIONAL SEARCH REPORT

In.	International Application No
PCT/US 93/09848	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 162 525 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.) 5 February 1986 cited in the application see claims 1-16 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 122 (C-168)(1267) 26 May 1983 & JP,A,58 042 602 (SANYO KASEI KOGYO K.K.) 12 March 1983 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 93/09848

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0317106	24-05-89	DE-A-	3878533	25-03-93
		JP-A-	1207327	21-08-89
EP-A-0248437	09-12-87	US-A-	4783510	08-11-88
		JP-A-	63099211	30-04-88
GB-A-2155020	18-09-85	JP-A-	60185550	21-09-85
		JP-A-	60185551	21-09-85
		JP-B-	3074241	26-11-91
		JP-A-	60186506	24-09-85
		JP-A-	60185804	21-09-85
		JP-A-	60185805	21-09-85
		CA-A-	1256640	27-06-89
		DE-A-	3507775	12-09-85
		FR-A,B	2560530	06-09-85
		US-A-	4666975	19-05-87
EP-A-0450924	09-10-91	US-A-	5164459	17-11-92
		AU-B-	634642	25-02-93
		AU-A-	7388991	03-10-91
		CN-A-	1056110	13-11-91
		JP-A-	4214735	05-08-92
GB-A-2162525	05-02-86	JP-B-	1017411	30-03-89
		JP-C-	1601163	31-01-91
		JP-A-	61016903	24-01-86
		JP-B-	4003411	23-01-92
		JP-A-	61097333	15-05-86
		JP-B-	4003412	23-01-92
		JP-A-	61101536	20-05-86
		DE-A,C	3523617	23-01-86
		FR-A-	2566786	03-01-86
		US-A-	4734478	29-03-88